

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C30B 23/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/28297</b> <b>(43) International Publication Date:</b> 7 August 1997 (07.08.97)
<b>(21) International Application Number:</b> PCT/US97/01292 <b>(22) International Filing Date:</b> 24 January 1997 (24.01.97) <b>(30) Priority Data:</b> 08/596,526 5 February 1996 (05.02.96) US <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> US 08/596,526 (CON) Filed on 5 February 1996 (05.02.96) <b>(71) Applicant (for all designated States except US):</b> CREE RE-SEARCH, INC. [US/US]; Suite 176, 2810 Meridian Park-way, Durham, NC 27713 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CARTER, Calvin, H. [US/US]; 114 N. Drawbridge Lane, Cary, NC 27513 (US); TSVETKOV, Valeri, F. [RU/US]; Apartment I, 717 Audubon Lake Drive, Durham, NC 27713 (US). GLASS, Robert, C. [US/US]; Apartment C5, 6123 Farrington Road, Chapel Hill, NC 27514 (US).	<b>(74) Agents:</b> SUMMA, Philip et al.; Bell, Seltzer, Park & Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US).  <b>(81) Designated States:</b> AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
<b>(54) Title:</b> GROWTH OF COLORLESS SILICON CARBIDE CRYSTALS  <b>(57) Abstract</b>  Large single crystals of silicon carbide are grown in a furnace sublimation system. The crystals are grown with compensating levels of p-type and n-type dopants (i.e., roughly equal levels of the two dopants) in order to produce a crystal that is essentially colorless. The crystal may be cut and fashioned into synthetic gemstones having extraordinary toughness and hardness, and a brilliance meeting or exceeding that of diamond.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

## GROWTH OF COLORLESS SILICON CARBIDE CRYSTALS

Field of the Invention

The invention relates to the growth of silicon carbide crystals. More particularly, the invention relates to the growth of transparent, monocrystalline, colorless silicon carbide crystals. Because of their durability and other advantageous physical and crystal properties, these crystals may be cut and fashioned into finished gemstones having the fire and brilliance of diamond.

10

Background of the Invention

Silicon carbide (SiC) is rarely found in nature. It has, however, been manufactured for more than eighty years, in crystalline form, for abrasive products. Silicon carbide crystals found in nature and in abrasive products are generally black and not translucent because they contain substantial levels of impurity atoms.

Because of the theoretically quite favorable electronic properties of silicon carbide, significant development activities were initiated during the 1960s and 1970s with the objective of growing large (bulk) crystals of low impurity silicon carbide for use in the production of semiconductor devices. These efforts finally resulted in the commercial availability of relatively low impurity, translucent silicon carbide crystals. These silicon carbide crystals are fabricated and marketed as very thin, green, amber or blue (175 $\mu$ m - 400 $\mu$ m) slices useful for semiconductor devices.

30

Recently, it has been discovered that relatively low impurity, translucent, single crystal silicon carbide may be grown with a desired color and thereafter cut and fashioned into synthetic gemstones.

-2-

These gemstones have extraordinary hardness, toughness, chemical and thermal stability, and a high refractive index that produces unparalleled brilliance. The single crystals from which the gemstones are produced  
5 have been grown by sublimation according to techniques of the type described in U.S. patent number Re. 34,061.

Silicon carbide crystals can be grown in a wide range of colors (including green, blue, red, purple, yellow, amber and black) and shades within each  
10 color by the appropriate selection of dopants (e.g., nitrogen and aluminum) and by varying the net doping densities (concentrations). Because of its wide bandgap, undoped ("intrinsic") silicon carbide crystals in the hexagonal or rhombohedral forms are inherently  
15 colorless. Thus, silicon carbide crystals offer the potential to be cut and fashioned into gemstones of many various appearances, including that of diamond.

Although the colored crystals have proven relatively easy to produce, problems have been  
20 encountered in creating the exceedingly impurity-free sublimation system environment necessary for growing undoped, colorless silicon carbide. Because colorless silicon carbide gemstones have an extraordinary appeal, there is a need for a more cost effective and reliable  
25 process for growing large single crystals of silicon carbide in colorless form.

#### Summary of the Invention

The present invention, in one broad aspect, is the discovery that large, transparent, colorless  
30 silicon carbide crystals may be grown in a sublimation system where compensating levels of n-type and p-type dopants are introduced into the crystals's lattice structure. The compensated levels of p-type and n-type dopants (i.e., roughly equal levels of the two dopants)  
35 serve to produce a colorless crystal by canceling each other in terms of the production of color centers in

- 3 -

the crystal. The compensation is best carried out at low carrier levels. For example, the preferred n-type dopant, nitrogen, may be introduced into the lattice only at those low levels dictated by "background" atmospheric nitrogen present in the sublimation system. A like amount of p-type dopant, e.g., aluminum, may be introduced via the sublimation powder or gas at a level sufficient to compensate for the background level of nitrogen. Thus, in one aspect, the present invention may be described as a colorless single crystal of silicon carbide grown with compensated levels of n-type and p-type dopants. These crystals may be cut and fashioned into brilliant colorless synthetic gemstones.

In another aspect, the invention may be defined as a method of producing a colorless single crystal of silicon carbide comprising the step of growing the single crystal of silicon carbide by a sublimation technique wherein compensated levels of p-type and n-type dopants are introduced into the crystal lattice structure.

#### Detailed Description of the Invention

It is to be understood at the outset of the description which follows that persons of skill in the appropriate arts may modify the invention as herein described while still achieving the favorable results of this invention. Accordingly, the description which follows is to be understood as being a broad, teaching disclosure directed to persons of skill in the appropriate arts, and not as limited upon the present invention.

Additionally, a number of the definitions, techniques and other aspects in the field of natural and synthetic gems and gemstones are well known to those of ordinary skill in this art. Relevant background and related information can be found, for example, in Volume 7 of the McGraw-Hill Encyclopedia of

-4-

Science & Technology, 7th Ed. (1992) at pages 651-659. It will be understood, of course, that this source is exemplary of the general knowledge in this art, rather than any limitation of the present invention.

5           In a preferred manner of practicing the invention, the growth of large, colorless single crystals of silicon carbide is achieved by introducing a polished monocrystalline seed crystal of silicon carbide of a desired polytype into the furnace of a  
10 sublimation system along with silicon and carbon containing source gas or powder (source material). The source material is heated to a temperature that causes the source material to create a vapor flux that  
15 deposits vaporized Si, Si<sub>2</sub>C, and SiC<sub>2</sub> to the growth surface of the seed crystal. The reproducible growth of a single selected polytype on the seed crystal is achieved by maintaining a constant flux of Si, Si<sub>2</sub>C and SiC<sub>2</sub>, and controlling the thermal gradient between the source material and the seed crystal. The growth  
20 procedure described above is set forth in more detail in U.S. patent number Re. 34,861, the teachings of which are incorporated entirely herein by reference.

          During the growth process of the present invention, roughly equal amounts of p-type and n-type  
25 dopants are maintained in the atmosphere of the sublimation furnace so that compensated levels of these two dopant types are introduced into the crystal lattice structure. In one preferred embodiment, the n-type dopant is nitrogen. The nitrogen source is the  
30 nitrogen present in the furnace atmosphere at "background" levels. Therefore, according to this embodiment, a p-type dopant, preferably aluminum, is added to the source powder in an appropriate amount so that the nitrogen and aluminum are incorporated into  
35 the crystal lattice structure in compensated amounts. In this regard, "compensated," "compensated amount," "compensated level," and like terms, are used to refer

-5-

to those roughly equal levels of p-type and n-type dopant atoms incorporated into the silicon carbide crystal lattice structure whereby the crystal is rendered essentially colorless.

5           In this regard, the terms "compensation" or "compensated" are also used in describing the electronic properties of a crystal, and likewise describes a semiconductor material that contains (frequently intentionally) both p and n-type dopants,  
10 including material in which one or the other predominates; e.g. a "compensated p-type material." Also, some uses refer to material in which p or n predominate as being "overcompensated" rather than simply "compensated." Thus, the terms "compensated"  
15 and "overcompensated" are familiar to those of ordinary skill in the semiconductor field.

It has been found desirable to compensate p-type and n-type dopants at low carrier levels. Thus, prior to initiating the sublimation growth process, the  
20 background level of atmospheric nitrogen in the furnace is desirably reduced to a relatively low level, for example, a level that will generally create an n-type dopant level in the crystal lattice on the order of about  $1 \times 10^{16}$  to  $1 \times 10^{18}$  atoms/cubic centimeter ( $\text{cm}^{-3}$ )  
25 with a more preferred range being between about  $1 \times 10^{17}$   $\text{cm}^{-3}$  x 5 to  $10^{17}$   $\text{cm}^{-3}$ . Reducing the level of atmospheric nitrogen in the furnace can be achieved by methods known in the art, typically, by backfilling with an inert gas such as argon, following by evacuating the  
30 furnace to very low pressure.

The compensated level of the p-type dopant is not absolutely critical provided it produces a crystal having sufficient colorless properties for the intended end use. Thus, broadly stated, the invention  
35 encompasses compensation that meets this goal, whether the dopant density is greater for the p-type or n-type dopant. It has been found desirable, however,

-6-

especially where the n-type dopant is nitrogen and the p-type dopant is aluminum, to have a greater density of aluminum atoms in the crystal lattice. Thus, in a preferred manner of practicing the invention, the level  
5 of aluminum atoms is in the range of one to five times that of the nitrogen atoms, with a more preferred range being one to two times.

The reasons for a somewhat greater density of p-type aluminum atoms are two-fold. First, p-type  
10 aluminum doping alone tends to impart a blue color to silicon carbide crystals, while n-type nitrogen doping alone tends to impart a green or amber color. Because colorless brilliance for gemstone applications is desired, a slight blue tint is preferable to a slight  
15 green or amber tint. Generally speaking, the preference arises from the aesthetic viewpoint that a blue tint is less detrimental than some other tint and, in some cases, is deemed desirable. The second reason for erring on the side of aluminum overcompensation is  
20 that aluminum is a deeper level dopant than nitrogen. Thus, at room temperature, the crystal will contain fewer active carriers due to an overcompensation of nitrogen. Because active carrier concentration is directly linked to the creation of color centers within  
25 the crystal, an overcompensation of aluminum is more likely to reduce the color of the crystal than will an overcompensation of nitrogen.

It will be appreciated that other dopants may be used, and that the dopants may be used at other  
30 densities. For example, the p-type dopant may be boron or beryllium, or other Group I, II or III elements. Similarly, other Group V elements may be used as n-type dopants in silicon carbide.

The present invention may be utilized to grow  
35 colorless crystals of different polytypes. In this regard, silicon carbide is a complex material system that forms more than 150 different polytypes, each



-7-

having different physical and electronic properties. The different polytypes can be classified in three basic terms: cubic, rhombohedral and hexagonal. Both the rhombohedral and hexagonal forms can occur in a number of different atomic arrangements that vary according to atomic stacking sequence. According to the invention, the preferred polytypes are 2H, 6H, 4H, 8H, 15R and 3C.

Large, colorless single crystals of silicon carbide grown by the techniques described above are ideally suited for use as gemstone materials. The colorless single crystals, if large enough, are first cut into a number of smaller pieces that serve as the rough gemstone material. The rough gemstones thereafter may be fashioned into finished gemstones by utilizing equipment currently employed in the art for fashioning diamonds and natural colored gemstones. Preferably, the silicon carbide gemstones of the invention are fashioned with precision diamond cuts to take advantage of the extraordinarily high refractive index of the silicon carbide material.

As noted earlier, those techniques required to turn an appropriate material into a final gemstone are generally well understood, and can be applied to the silicon carbide material of the present invention without undue experimentation.

Although the invention has been described in connection with certain embodiments, it will be appreciated that modifications may be made without departing from the true spirit and scope of the invention.

-8-

## THAT WHICH IS CLAIMED IS:

1. A synthetic gemstone formed from a colorless, single crystal of silicon carbide containing compensated levels of n-type and p-type dopants.
2. A synthetic gemstone as claimed in Claim  
5 1 wherein the n-type dopant comprises nitrogen.
3. A synthetic gemstone as claimed in Claim  
2 wherein nitrogen atoms are present in the crystal at a concentration dictated by background levels of nitrogen in the sublimation system.
- 10 4. A synthetic gemstone as claimed in Claim  
2 wherein the n-type dopant comprises aluminum.
5. A synthetic gemstone as claimed in Claim  
4 wherein the concentration of aluminum atoms is in the range of about one to five times that of nitrogen  
15 atoms.
6. A synthetic gemstone as claimed in Claim  
4 wherein the concentration of aluminum atoms is between about one and two times the concentration of nitrogen atoms.
- 20 7. A colorless single crystal of silicon  
carbide grown with compensated levels of n-type and p-type dopants.
8. A synthetic gemstone according to Claim 7  
or Claim 10 wherein the polytype of the silicon carbide  
25 single crystal is selected from the group consisting of  
2H, 6H, 4H, 8H, 15R and 3C.

-9-

9. A colorless single crystal of silicon carbide according to Claim 1 or Claim 7 wherein each dopant type is present in the crystal at a concentration of between about  $1 \times 10^{16} \text{ cm}^{-3}$  and  $1 \times 10^{18}$   
5  $\text{cm}^{-3}$ .

10. A colorless single crystal of silicon carbide according to Claim 1 or Claim 7 wherein each dopant type is present in the crystal at a concentration of between about  $1 \times 10^{17} \text{ cm}^{-3}$  and  $5 \times 10^{17}$   
10  $\text{cm}^{-3}$ .

11. A colorless single crystal of silicon carbide as claimed in Claim 9 wherein the n-type dopant comprises nitrogen and the p-type dopant comprises aluminum.

12. A method of producing a colorless single crystal of silicon carbide comprising growing the single crystal of silicon carbide by a sublimation technique while introducing compensated levels of p-type and n-type dopants into the crystal lattice  
15 structure.

13. A method as claimed in Claim 12 wherein the n-type dopant comprises nitrogen and the sublimation technique incorporates a furnace having an atmosphere containing nitrogen only at background  
20 levels, and including the step of introducing the p-type dopant at a compensated level roughly equivalent to the amount of nitrogen introduced into the crystal due to the atmospheric background presence of nitrogen.

14. A method as claimed in Claim 13 wherein  
30 the p-type dopant comprises aluminum and including the step of introducing aluminum atoms into the crystal lattice structure at a concentration from about one to

-10-

five times the concentration of nitrogen atoms in the lattice structure.

15. A method as claimed in Claim 13 wherein the p-type dopant comprises aluminum and including the  
5 step of introducing aluminum atoms into the crystal lattice structure at a concentration from about one to two times the concentration of nitrogen atoms in the lattice structure.

16. A method as claimed in Claim 12 wherein  
10 each dopant type is present in the crystal at a concentration of between about  $1 \times 10^{16} \text{ cm}^{-3}$  and  $1 \times 10^{18} \text{ cm}^{-3}$ .

17. A method as claimed in Claim 14 wherein  
15 each dopant type is present in the crystal at a concentration of between about  $1 \times 10^{17} \text{ cm}^{-3}$  and  $5 \times 10^{17} \text{ cm}^{-3}$ .

18. A method according to Claim 12 wherein the sublimation technique comprises:

introducing a monocrystalline seed crystal of  
20 silicon carbide of desired polytype and a silicon carbide source powder into a sublimation system;

raising the temperature of the silicon carbide source powder to a temperature sufficient for the source powder to sublime; while

25 elevating the temperature of the growth surface of the seed crystal to a temperature approaching the temperature of the source powder, but lower than the temperature of the source powder and lower than that at which silicon carbide will sublime  
30 under the gas pressure conditions of the sublimation system; and

generating and maintaining a substantially constant flow of vaporized Si, Si<sub>2</sub>C, and SiC<sub>2</sub> per unit

-11-

area per unit time from the source powder to the growth surface of the seed crystal for a time sufficient to produce a desired amount of macroscopic growth of monocrystalline silicon carbide of desired polytype

5 upon the seed crystal; and

maintaining levels of p-type and n-type dopant atoms in the sublimation system sufficient to introduce compensated levels of the two dopant types into the crystal lattice structure.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/01292

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C30B23/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF CRYSTAL GROWTH, vol. 115, no. 1 / 04, 2 December 1991, pages 733-739, XP000322885 WOO SIK YOO ET AL: "BULK CRYSTAL GROWTH OF 6H-SIC ON POLYTYPED-CONTROLLED SUBSTRATES THROUGH VAPOR PHASE AND CHARACTERIZATION" see page 735, right-hand column see page 736, right-hand column see page 737, left-hand column ---	1-4,7,8, 12
A	US RE34861 E (DAVIS ROBERT F ET AL) 14 February 1995 see claim 1 -----	18

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*&\* document member of the same patent family

Date of the actual completion of the international search

3 June 1997

Date of mailing of the international search report

19. 06. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Flink, E

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/01292

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US RE34861 E	14-02-95	US 4866005 A	12-09-89
		CA 1331730 A	30-08-94
		DE 3855539 D	17-10-96
		DE 3855539 T	23-01-97
		EP 0389533 A	03-10-90
		EP 0712150 A	15-05-96
		JP 3501118 T	14-03-91
		WO 8904055 A	05-05-89
-----			